

REACTIONS OF MUSTARD ON CONCRETE

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ABSTRACT

The reactions of the blister agent mustard, (bis(2-chloroethyl) sulfide, HD) were monitored on concrete substrates. The CDCl_3 extract of concrete monoliths was analyzed using both NMR and GC/MSD; the percent HD extracted depended upon its contact time with the concrete before extraction. Vinyl, hydroxyl, and sulfoxide products were detected. ^{13}C SSNMR measurements of HD* on the concrete substrates indicated a strong interaction between the HD* and the concrete that has silica filler; the interactions between the HD* and the two concretes that had limestone filler were weak. ^{13}C SSNMR measurements of HD* on concrete showed that hydrolysis products were present after six days of exposure time.

INTRODUCTION

Knowledge of when a CWA (Chemical Warfare Agent) no longer poses a hazard – that is, when a contaminated area is safe to enter without protective clothing – is of major concern for battlefield commanders. Decisions must be made whether to decontaminate an area, or if natural weathering alone will allow resumption of normal operations after an acceptable waiting period.

Mustard (bis(2-chloroethyl) sulfide), has previously been shown to persist for four years on soil. It hydrolyzed and polymerized to form toxic CH-TG¹ and H-2TG² over this period of time.³ Prior studies of the extraction of mustard from concrete using isopropanol or acetonitrile and GC/MS analysis of the solvent showed 0 to 67% recovery of mustard.

In the current study, extraction and in situ NMR techniques were applied to investigate the persistence and reactivity of CASARM grade (HD) and ^{13}C -labeled (HD*) mustard on three types of concrete.

EXPERIMENTAL

2.1 SUBSTRATES

One concrete sample was made with 3 mm silica filler and aged (ASF); the other two concrete samples were runway concrete formulations made with limestone filler and were obtained from the Army Corps of Engineers. One was made with low-iron cement (abbreviated LIFL, low-iron limestone filler),

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and the other was obtained from a core sample of a used runway (abbreviated AULF, for aged used limestone filler). The ASF concrete was used ambient and after conditioning for two weeks at 80% relative humidity. The LILF and AULF concretes were used under ambient conditions.

2.2 EXTRACTION OF HD FROM CONCRETE

Four 1 μ L drops of CASARM (Chemical Agent Standard Analytical Reference Material) grade HD ($\text{ClCH}_2\text{CH}_2\text{S}$) were placed onto 5 mm x 9 mm x 15 mm monoliths of ambient ASF concrete. After exposure times of 1, 8, and 24 hours, at 22°C the samples (run in triplicate) were extracted with 4 mL CDCl_3 , crushed, and re-extracted with 2 mL CDCl_3 . A similar experiment was performed with HD* on ASF that had been conditioned at 80% RH and 22°C for two weeks. After exposure times of 1, 8, 24, 48, 72, and 401 hours the monoliths (run in duplicate) were crushed and extracted once with 2 mL CDCl_3 . The extracts were analyzed using GC/MSD, and liquids ^{13}C and ^1H NMR. Two-dimensional ^1H - ^{13}C (HMBC, HMQC) and ^1H - ^1H (COSY) NMR studies of the extract were also used to identify products.

2.3 SOLID STATE MAGIC ANGLE SPINNING (SSMAS) NMR OF HD* ON SUBSTRATES

Each substrate was ground into a fine powder and packed into a 5 mm diameter x ~10 mm length sample area of a solid state NMR rotor. One 4 μ L drop of HD* was injected onto the powder, and the sample was capped. The samples were spun at ~2000 Hz in a 400 MHz Varian Inova NMR instrument. All concrete samples were used under ambient conditions.

RESULTS AND DISCUSSION

3.1 EXTRACTION OF HD FROM ASF

The percentage of HD recovered decreased as the contact time increased. It was determined that removal of the HD from the one-hour contact time samples was quantitative after two extractions; thus, the same protocol was followed for all of the ambient samples. The amended protocol gave quantitative extractions for the one-hour samples, and thus was used for all of the conditioned samples. The GC/MSD and NMR techniques showed the same trend for the total amount of material extracted, although the GC method generally gave higher percent recoveries than the NMR technique did.

Seven different products were found by using two detection techniques. It was often difficult to detect thioglycol using the GC/MSD technique, and thus it was only identified in the NMR. Many of the compounds observed in the GC were not detected in the NMR. This is likely due to the amount of compound present; a more concentrated solution and/or longer NMR acquisition times would probably reveal these compounds.

The products show that hydrolysis of the Cl, oxidation of the S, and reduction of the ethyl group to vinyl all occur. In addition, these species dimerized to form other compounds, such as Q, which is $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$.

More material was extracted from the conditioned concrete than the ambient samples. For example, after 24 hours a total of 50.8% of the original HD was obtained from the ambient ASF samples, and 4.4% was due to products. By contrast, a total of 85.2% was extracted from the conditioned sample, and 14.0% was products. Thus, the moister concrete has more HD that is available for extraction and reaction. The interpretation of this observation is that the moisture coats the pores of the concrete, thus the mustard is less able to absorb to the surface. In addition, the presence of the moisture resulted in a greater rate of hydrolysis.

TABLE 1. Percent HD Extracted from Ambient ASF Concrete based on NMR Data

Hours	First Extract		Second Extract		% Total
	%HD	%Products	%HD	%Products	
1	75.3	0.0	26.0	0.0	101.3
8	58.0	0.0	9.0	0.0	67.0
24	18.7	2.0	27.7	2.4	50.8

TABLE 2. Products Found in Extracts of ASF after 24-hour Exposure to HD

Both Techniques
2-hydroxyethyl vinyl sulfide, CH ₂ =CHSCH ₂ CH ₂ OH
Bis(2-chloroethyl) sulfoxide, ClCH ₂ CH ₂ SOCH ₂ CH ₂ Cl
NMR
Thiodiglycol, HOCH ₂ CH ₂ SCH ₂ CH ₂ OH (TDG)
GC/MSD
2-chloroethyl vinyl sulfide, CH ₂ =CHSCH ₂ CH ₂ Cl
2-chloroethyl-2-hydroxyethyl sulfide, ClCH ₂ CH ₂ SCH ₂ CH ₂ OH
Q, ClCH ₂ CH ₂ SCH ₂ CH ₂ SCH ₂ CH ₂ Cl
HD-disulfide, ClCH ₂ CH ₂ SSCH ₂ CH ₂ Cl

TABLE 3. Percent HD Extracted from 80% RH Conditioned ASF Concrete based on NMR Data

Hours	%HD	%Products	Total %Extracted
1	95.5	1.8	97.3
8	85.9	7.8	93.7
24	71.2	14.0	85.2
48	52.0	13.0	65.0
72	38.2	15.9	54.2
401	2.1	3.2	5.3

3.2 HD* ON CRUSHED SUBSTRATES

The ASF substrate exhibited very strong spinning side bands; the main peaks accounted for only 50% of the overall total integrated peak areas. Strong spinning side bands are generally indicative of a high degree of order in the substrate; in this case the interpretation is that the strong spinning side bands imply strong binding between the HD* and the substrate. A further implication is that the materials that have weak spinning side bands will have a higher vapor hazard; this needs to be verified by an independent technique.

Monitoring of the samples over a period of three weeks showed the presence of hydrolysis products formed from HD* on the LILF concrete. Products were not observed on the AULF and ASF samples during this period of time. Detection of products on the ASF sample thus far has been difficult due to the intensity of the spinning side bands, which obscure any product peaks. Monitoring of these samples will continue for several months.

TABLE 4. Percentage Total Integrated Peak Area in Main Peaks for HD* on Various Substrates

Crushed Substrate	% Intensity in Main Peaks
ASF	50
AULF	73
LILF	95

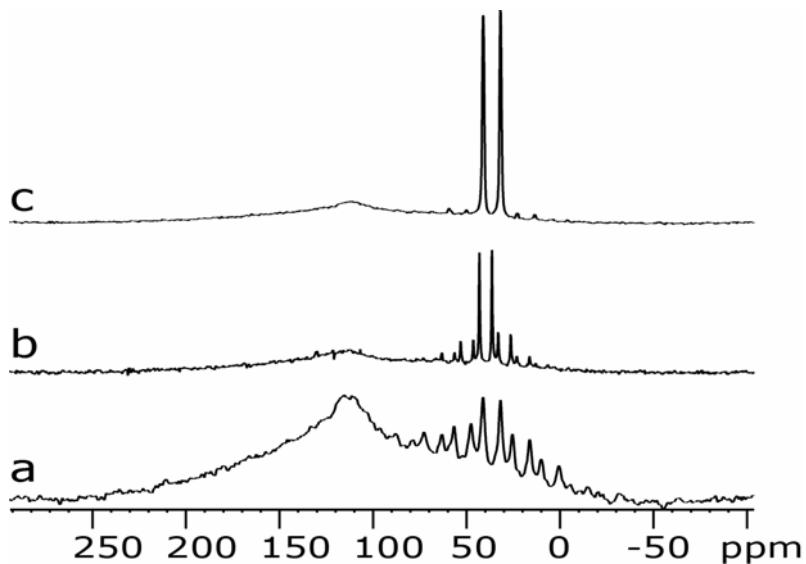


Figure 1. ^{13}C NMR SSMAS spectrum of 4 μL of HD* on crushed: a) ASF, b) AULF, and c) LILF concrete.

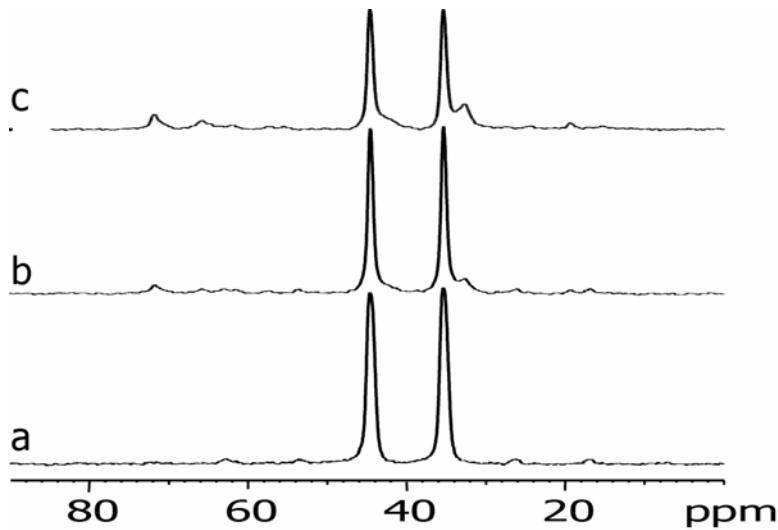


Figure 2. Initial (a), 6-day (b), and 20-day (c) ^{13}C SSMAS spectra of HD* on crushed LILF concrete.

CONCLUSIONS

Mustard ($\text{ClCH}_2\text{CH}_2)_2\text{S}$ that was placed onto ambient ASF concrete samples formed vinyl, hydroxyl, S-oxidized and dimerized species after a period of 24 hours; these were seen after 8 hours on conditioned ASF concrete. The presence of moisture increased the rate of formation of the products.

Concrete from various sources exhibited different reactivity towards the HD*. It was difficult to see products on the ASF concrete easily due to the numerous spinning side bands. Products were observed on the crushed LILF concrete in six days.

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REFERENCES

¹ CH-TG is $\text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S}^+(\text{CH}_2\text{CH}_2\text{OH})_2\text{Cl}^-$.

² H-2TG is $\text{S}(\text{CH}_2\text{CH}_2\text{S}^+(\text{CH}_2\text{CH}_2\text{OH})_2\text{Cl}^-)_2$.

³ Wagner, G. W. and MacIver, B. K. 1998: Degradation and Fate of Mustard in Soil as Determined by ^{13}C MAS NMR, *Langmuir*, **14**, 6930-6934.